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(54) USE OF TERTIARY NITROGEN-CONTAINING CELLULOSE ETHERS AS AGGREGATING AGENTS

(71) We, MODOKEMI AB, a Swedish Body Corporate, of S—444 01 Stenungsund 1, Sweden,

do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the use of tertiary nitrogen-containing cellulose ethers as aggregating agents, in particular, to the use of such ethers in the cellulose and paper industry.

Tertiary nitrogen-containing cellulose ethers are well known and due to their electropositive charge they have been used primarily as fixing agent for water-soluble acidic dyes on textiles and paper. Other suggested fields of application are as components in coating and adhesive compositions and as impregnating and finishing agents in the manufacture of textiles. Despite the great number of suggested uses, however, the tertiary cellulose ethers have had only marginal use.

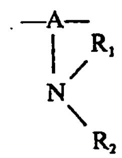
Quaternary nitrogen containing cellulose ethers are also known and suggested uses for these are as flocculating and thickening agents and as textile and paper-making aids. Investigations have proved, however, that the quaternary nitrogen containing compounds as compared to hitherto usually employed flocculating agents, such as those based on polyacrylamide, have a relatively low flocculating capacity and that moreover their production is relatively difficult and time-consuming.

Surprisingly, it has been found that tertiary nitrogen containing compounds have a very significant effect as aggregating agents. "Aggregating agents" as used herein refers to agents which in a system comprising particles suspended and/or colloidally dissolved in a liquid enable the particles to attract each other, mainly by the intermediary of interparticulate surface reactions, thereby to form larger aggregates of the suspended or colloidally dissolved particles. Aggregation in the sense of this definition occurs in processes such as flocculation, coagulation, precipitation, dewatering and flotation, which are utilized in a number of industrial processes. Thus, aggregating agents according to this invention may be used e.g. as retention aids in paper making and in the manufacture of sheet materials from organic or inorganic fibres starting material, such as building boards comprising mineral fibres, in the purification of aqueous effluents e.g. raw water and industrial or domestic waste water or sewage, e.g. containing fibres and other solids, in the flotation and enrichment of minerals and in flocculating and precipitating processes in the textile and food industries.

The present invention provides a method of aggregating particles wherein a suspension or colloidal solution containing solid particles is brought into contact with a tertiary nitrogen-containing cellulose ether having a degree of polymerization of 100—5000 and containing substituents of the general formula:

$$-(C_aH_{2a}O)_m-\left[\begin{array}{l} A \\ | \\ N\begin{array}{l} \diagup R_1 \\ \diagdown R_2 \end{array} \end{array}\right]_n-(C_bH_{2b}O)_p-(C_cH_{2c})_q-R_3$$

where a and b, which may be the same or different each is 2, 3 or 4, c is an integer from 1 to 20; m and p, which may be the same or different each is 0, 1, 2 or 3; n is 0, 1, 2, 3, 4 or 5; q is 0 or 1; A represents a hydrocarbon residue A_1 having 1 to 5 carbon atoms or A_1—O—, where A_1 is as defined above, A_1 being optionally substituted by one or more hydroxyl groups; R_1 and R_2, which may be the same or different each represents a hydrocarbon group having 1 to 10 carbon atoms, or a substituted hydrocarbon group containing 1 to 10 carbon atoms and having one or more ether linkages and/or one or more primary, secondary or tertiary amino groups, or R_1 and R_2 together with the nitrogen atom to which they are linked represents a heterocyclic ring containing one or more hetero atoms of which at least one is nitrogen; and R_3 represents hydrogen, $CONH_2$ or CN or COOH or a salt thereof, said cellulose ether being one in which the number of nitrogen atoms from the group



per anhydroglucose unit is 0.01—1.0 the average number of $CONH_2$, CN or COOH groups per anhydroglucose unit is 0 to 1.0 and the average of m+p+q is 0.5—5.0, preferably 0.8—2.0.

The cellulose ether used in this invention provides, above all, an excellent retention in paper making with very little tendency for non uniform aggregation, so-called cloudiness, even at high added amounts. The cellulose ethers wherein R_3 designates hydrogen, $CONH_2$ or CN, have been found to possess particularly good properties as retention agents for unsized paper, while cellulose ethers containing anionic groups, such as COOH groups or salts thereof, show particularly advantageous effects in the presence of, e.g., Al^{3+} ions, so that they provide good retention in the manufacture of various types of sized papers. The reason why the cellulose ethers containing carboxyl groups have these special properties is not fully explained, but it is believed that it is related to the amphoteric character of these cellulose ethers and their consequent affinity for Al^{3+} and other ions. Most preferred cellulose ethers are those wherein a and b independently designate the integer 2, 3 or 4; preferably 2; c designates an integer from 1 to 4, preferably 2; m and p designates 0 or an integer from 1 to 3; q is 0 or 1; n is 0 or 1 (n may be zero in some substituents but not all substituents since the average number of nitrogen atoms from the

group per anhydroglucose unit must be 0.01—1.0); A designates a hydrocarbon residue containing 1 to 5 carbon atoms; R_1 and R_2 independently designate hydrocarbon groups having 1 to 5 carbon atoms; and R_3 designates hydrogen, the average number of nitrogen atoms per anhydroglucose unit being 0.01—1.0, preferably 0.1—0.5, and the average of m+p+q being 0.5—5.0, for example 0.5—3.0 or 0.8 to 2.0 and preferably 0.8 to 3.0. It has been found in numerous experiments, that cellulose ethers used in the invention, which come within this definition, consistently provide a very high retention in the manufacture of unsized paper. Generally, the retention agents commonly used provide substantially lower retention for unsized paper than for sized papers, which is believed to be due to the fact that in sized paper the retention is facilitated by the presence of size additives and other aids. Therefore, it is surprising that the cellulose ethers defined above in many cases impart to unsized paper a retention which is practically as high as in the case of sized paper.

The cellulose ethers used in this invention may be prepared by introducing, by methods well known per se, into the cellulose molecule chain nonionic and cationic groups and, optionally, anionic groups. The various necessary reactants

may be added simultaneously or in any sequence, and the various substituent groups may be introduced into the cellulose chain under conditions which are usual in such reactions. The starting material for preparing the cellulose ethers is suitably pure cotton, cotton linters or pure wood cellulose. Of course, it is also possible to start from suitable commercially available cellulose ethers, such as methylcellulose hydroxyethyl-cellulose, hydroxypropyl-cellulose, methyl-hydroxy-ethyl-cellulose, ethyl-hydroxy-ethylcellulose, hydroxyethyl-hydroxypropyl-cellulose, ethyl-hydroxyethyl-hydroxy-propylcellulose, carboxymethylcellulose, carboxymethyl-hydroxyethylcellulose, methyl-carboxymethylcellulose or ethyl-carboxymethylcellulose or salts thereof.

In order that the reactants shall react in a simple manner with the cellulose to introduce suitable substituent groups, the cellulose should be activated by mercerization with an alkali metal hydroxide solution, such as sodium hydroxide, having a concentration of 5 to 30% by weight, preferably 18 to 23% by weight. After mercerization the cellulose is squeezed to press factor of 2.0 to 3.5, preferably 2.0—3.0. The term "press factor" refers to the ratio between the weight of pulp and sodium hydroxide solution after squeezing and the weight of the air-dry starting pulp prior to mercerization. Thereupon, the mercerized cellulose is easily reacted with a great number of reactants, when suitable reaction conditions are employed. In these reactions, it is suitably in finely-divided form, slurried or suspended in a reaction medium, which may be water, dioxan, xylene, dichloromethane, pentane, acetonitrile, ethyl chloride, propyl chloride, butyl chloride, petroleum ether or hexanol or mixtures of two or more of these reaction media. It is also possible to dissolve the mercerized cellulose, e.g. in dimethyl sulfoxide and react the cellulose in this form with suitable reactants. To introduce the nonionic groups well-known etherifying agents, such as methyl chloride, ethyl chloride, propyl chloride, butyl chloride, ethylene oxide, propylene oxide, butylene oxide, acrylamide and acrylonitrile, may be used. The carboxylic acid group or its salt may suitably be introduced by the use of monochloroacetic acid, sodium chloroacetate and chloropropionic acid as etherifying agents. It is also possible to introduce carboxylic acid groups by reacting the cellulose with acrylamide or acrylonitrile and subjecting the groups thus introduced to a subsequent acidic or alkaline hydrolysis step. The tertiary amino group may be introduced by reacting the anhydroglucose unit with a compound of the general formula

$$X\text{—}A\text{—}N\begin{matrix}\diagup R_1 \\ \diagdown R_2\end{matrix}$$

wherein X designates a halogen atom or an inorganic ester group, e.g. HSO_3, and A, R_1 and R_2 are as defined above. The tertiary compound is preferably used in the form of a salt of an inorganic acid, such as the hydrochloride salt. Specific aminating agents which can be used according to the invention, include e.g. 2-chloroethyldiethylamine hydrochloride 2-chloroethyldimethylamine hydrochloride, N-(2-chloroethyl)-N-methyl-N′-dimethylethylenediamine dihydrochloride, N-(2-chloroethyl)piperazine dihydrochloride, N-(2-chloroethyl)-N′-methylpiperazine dihydrochloride, 4-chloro-2-butenyldimethylamine hydrochloride, 2-sulfoethyldiethylamine sulfate, 3-chloro-2-hydroxypropyldiethylamine hydrochloride and 2,3-epoxypropyldiethylamine hydrochloride. In the case where the aminating agent is an epoxide, the reaction may be carried out in the presence of catalytic amounts of alkali.

After completed reaction, the cellulose ethers according to the invention may, if desired, be subjected to a washing step. Any alkali remaining after purification may, if desired, be neutralized with a suitable acid, such as phosphoric acid, whereupon the product is dried and ground to the desired particle size.

Before use, the cellulose ether is dissolved in water and small amounts of a biocide or an antioxidant may be added thereto. The solids content of the solution may of course be varied considerably, depending on the intended use, but will usually be 0.01—5% by weight, preferably 0.1 to 2% by weight. For use as a retention agent in paper-making a 0.05 to 2.0% solution will usually be added in an amount such that the amount of cellulose ether will be at least 10 grams, preferably at least 50 grams, and not above 2000 grams, preferably not above 600 grams per ton of dry cellulose pulp. For sized paper and paperboard, it is usually preferable

to use somewhat higher proportions of cellulose ether than for unsized paper. For flocculation, flotation, coagulation, precipitation and dewatering purposes, e.g. in the purification of waste-water or raw water, the cellulose ether is suitably added in such an amount that the concentration thereof will be 0.01—100 ppm. Based on the quantity of solids to be flocculated it will usually be from 10 to 1000 grams per ton of solids.

The following examples serve to illustrate the invention. In these examples, all viscosity values indicated have been determined in a 1% solution with a Brookfield viscometer, (type LVT), 12 rpm, while the indicated retention values have been obtained by preparing hand-made sheets. The retention test was carried out by dewatering an aqueous suspension, which per liter contained 2.8 g of bleached sulfate pulp and 0.84 g of kaolin pigment (English china clay, grade C) and for sized paper additionally 0.014 g of resin soap and 0.084 g of alum as sizing component, through a wire screen having a mesh width of 0.15 mm and a wire diameter of 0.10 mm. The retention was measured as the amount of kaolin pigment in the sheet relatively to the charged amount.

Example 1.

Cotton linters (40 g) were mercerized in a 21% aqueous sodium hydroxide solution for 30 minutes at room temperature. The mercerized cellulose was squeezed to a press factor of 2.4, whereupon the resulting alkali cellulose was shredded to a fluffy mass, which was immediately transferred to an autoclave. After evacuation of the autoclave to remove all air present therein, 60 g of ethyl chloride and 24.4 g of ethylene oxide were introduced by means of the sub-atmospheric pressure in the autoclave. With thorough agitation, the temperature of the reaction mixture was continuously increased during 75 minutes to 105°C, whereupon the charge was allowed to react at this temperature for 75 minutes more. Thereupon, the contents of the autoclave were cooled to 30°C, and 20 g of 46% aqueous sodium hydroxide solution was added followed by 17 g of pulverulent 2-chloroethyldiethylamine hydrochloride, whereupon the charge was kept at 30°C for 60 minutes. The resulting product was washed in water of about 95°C and neutralized with dilute aqueous acetic acid to a pH of about 7, whereupon it was dried at 50 to 70°C and ground. The resulting final product consisted of diethylaminoethyl substituted ethyl-hydroxyethylcellulose having $DS_{ethyl}=0.9$, $MS_{hydroxyethyl}=1.0$, and $DS_{diethylaminoethyl}=0.13$, and having a viscosity of 5680 cP. (DS is the degree of substitution, MS is molecular substitution). For unsized paper the cellulose ether gave a retention effect of 81%, and the corresponding value for sized paper was 82%. For comparison it may be mentioned that with no addition unsized paper gave a retention of 20% and sized paper a retention of 52%, which shows that the cellulose ether of this example is an excellent retention agent.

Example 2.

Cotton linters (40 g) were mercerized in 20% aqueous sodium hydroxide at room temperature for 30 minutes, whereupon the mercerized cellulose was squeezed to a press factor of 2.5. The resulting alkali cellulose was shredded to a fluffy mass, which was immediately transferred to an autoclave. After removing air present in the autoclave by evacuation, 60 g of ethyl chloride and 38 g of ethylene oxide were introduced into the autoclave by the aid of the vacuum. The autoclave charge was mixed thoroughly while the temperature was raised to 50°C and maintained at this value for 60 minutes. Thereupon the reaction mixture was cooled to 30°C and 17 g of 2-chloroethyldiethylamine hydrochloride added, whereupon the mixture was allowed to react at 30°C for 60 minutes. The reaction product which contained about 40% salts, was purified from these salts by repeated washing in acetone/water, neutralized with dilute aqueous acetic acid to a pH of about 7, dried at 50—70°C and ground to a powder. The resulting diethylaminoethyl substituted hydroxyethylcellulose had $MS_{hydroxyethyl}=1.6$ and $DS_{diethylaminoethyl}=0.14$ and a viscosity of 3310 cP. The retention was 80% for unsized paper and 84% for sized paper, which shows that the cellulose ether can be used to advantage as a retention aid.

Example 3.

An autoclave was charged with 34 g of hydroxyethylcellulose (viscosity about 2500 cP; molecular substitution about 2.5) together with 290 g of hexane. Thereupon, 15 g of sodium hydroxide dissolved in 45 g of water was added, whereupon air was removed from the autoclave by evacuation and the charge

mixed for 30 minutes at room temperature. Then, 5.6 g of N-(2-chloroethyl)-piperazine dihydrochloride was added, and after renewed evacuation to remove any additional air, the autoclave charge was heated to 85°C and maintained at this temperature for 3 hours. The resulting mixture was rendered free of salts by repeated washing in acetone/water, and was then neutralized with acetic acid to a pH of about 7, dried at 50—70°C and ground. The final product was a piperazinoethyl substituted hydroxyethylcellulose having $MS_{hydroxyethyl}=2.5$ and $DS_{2\text{-}piperazinoethyl}=0.13$. The viscosity of the cellulose ether was 53 cP. The retention effect was determined to 73% for unsized paper and 75% for sized paper.

Example 4.

Addition of ethylene oxide to cellulose was carried out in the manner described in Example 2. Thereupon, 17 g of 2-chloroethyldiethylamine hydrochloride was added, and the mixture was allowed to react at 30°C. After 30 minutes 7 g of acrylamide was added, and the reaction was allowed to proceed at the same temperature for 45 minutes more. The reaction product was washed repeatedly in acetone/water to remove salts, whereupon it was neutralized with acetic acid to a pH of about 7, dried and ground. The final product, which consisted of hydroxyethylcellulose containing both diethylaminoethyl and carbamoylethyl substituents, had $MS_{hydroxyethyl}=1.6$, $MS_{diethylaminoethyl}=0.08$ and $DS_{carbamoylethyl}=0.18$. The viscosity of the cellulose ether was 4250 cP, and its retention effect was determined to 74% for unsized paper and 76% for sized paper.

Example 5.

A cellulose ether was prepared in the same manner as in Example 4, except that prior to the neutralization with acetic acid the temperature was raised to about 70°C. At this temperature, a partial hydrolysis of the carbamoylethyl groups to form carboxyethyl groups occurred. After 1 hour, the hydrolysis was terminated by lowering the temperature to room temperature, and in this period about 75% of the carbamoylethyl groups had been hydrolyzed. The resulting cellulose ether had a substitution of $MS_{hydroxyethyl}=1.6$, $DS_{diethylaminoethyl}=0.08$, $DS_{carbamoylethyl}=0.05$, $DS_{carboxyethyl}=0.13$. The viscosity of the cellulose ether was 5660 cP, and its retention was determined to 68% for unsized paper and 81% for sized paper. The high retention effect obtained on sized paper as compared to the corresponding value for unsized paper is remarkable.

Example 6.

An autoclave containing 40 g of hydroxypropylcellulose (viscosity 2000 cP, $MS_{hydroxypropyl}=1.1$) was charged with 0.4 mol of 2-chloro-ethyldiethylamine hydrochloride per mol of anhydroglucose unit. After reaction at 50°C for 30 minutes, the product was washed and neutralized with concentrated acetic acid in water of 90°C. The resulting diethylaminoethyl substituted hydroxypropylcellulose had a diethylamino substitution of 0.15 and a viscosity of 1040 cP. The retention was measured to 77% on unsized paper and to 78% on sized paper, which shows that the cellulose ether had good retention throughout.

Example 7.

An autoclave containing 40 g of ethyl-hydroxyethyl-hydroxypropylcellulose (viscosity 7000 cP, $MS_{hydroxyethyl}=0.5$, $MS_{hydroxypropyl}=0.8$, $DS_{ethyl}=0.7$) was charged with 0.2 mol of 2-chloroethyldiethylamine hydrochloride per mol of anhydroglucose unit and 20 g of 45% aqueous sodium hydroxide. Amination was carried out at 50°C for 30 minutes, whereupon the reaction was stopped, and the resulting product was washed and neutralized with concentrated acetic acid in water of 90°C. The final product had $DS_{diethylaminoethyl}=0.18$ and a viscosity of 3420 cP. The retention effect was determined to 79% for unsized paper and 78% for sized paper, which is to be considered as a good retention effect.

Example 8.

In the same way as in Example 2, mercerized cotton linters were reacted with ethylene oxide and an aminating agent, the amount of ethylene oxide being 4.0 mols per mol of anhydroglucose unit and the aminating agent being 2,3-epoxypropyldiethyl amine which was added in an amount of 0.4 mol per mol of anhydroglucose unit. After purification and working up, a final product was

obtained which had a viscosity of 3760 cP and a substitution of $MS_{hydroxyethyl}=1.8$ and $DS_{3\text{-diethylamino-2-hydroxypropyl}}=0.14$. The retention of the cellulose ether was 85% for unsized paper and 86% for sized paper, showing that the cellulose ether is an excellent retention agent.

Example 9.

In this example, a comparison is made between the retention effect of a cellulose ether according to this invention and that of a corresponding cellulose ether having a quaternary instead of the tertiary nitrogen substituent. Hydroxyethylcellulose ($MS_{hydroxyethyl}=1.8$, viscosity 3500 cP was mixed with 2-chloroethyldiethylamine hydrochloride in proportion of 0.4 mol per mol of anhydroglucose unit, and the compounds were reacted under the same conditions as in Example 2. For comparison a corresponding cellulose ether containing quaternary nitrogen was prepared. Thus, 40 g of the same hydroxyethylcellulose was reacted with 2,3-epoxypropyltrimethylammonium chloride in a proportion of 0.4 mol per mol of anhydroglucose unit together with 750 g of acetonitrile at 50°C for about 16 hours. After filtration of the reaction mixture and washing of the filter cake twice with acetonitrile and twice with acetone, a product was obtained which had $DS_{3\text{-trimethylamino-2-hydroxypropyl}}=0.17$. The two products were tested with regard to retention effect on both sized and unsized paper. The following results were obtained.

Substitution	Retention (%)	
	Sized paper	Unsized paper
$MS_{hydroxyethyl} = 1.6$ $DS_{diethylaminoethyl} = 0.14$	80	84
$MS_{hydroxyethyl} = 1.6$ $DS_{3\text{-trimethylamino-2-hydroxypropyl}} = 0.17$	53	63

It is apparent that the cellulose ether according to this invention in spite of lower nitrogen substitution provides a considerably better retention for both unsized and sized paper.

Example 10.

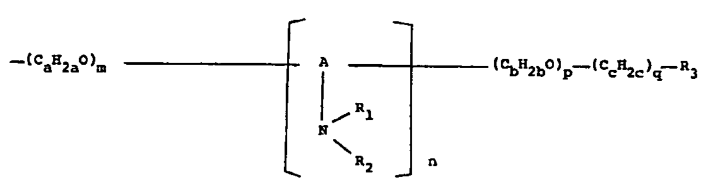
A 1% homogenized suspension of kaolin in water was introduced into the measuring cell of a photometer. A 0.2% aqueous solution of a flocculating agent which consisted of a polyethyleneimine or a cationic starch or a cellulose ether having $MS_{hydroxyethyl}=1.8$, $DS_{diethylaminoethyl}=0.16$, $DS_{carbamoylethyl}=0.15$ or a cellulose ether having $MS_{hydroxyethyl}=1.8$, $DS_{diethylaminoethyl}=0.16$ and $DS_{ethyl}=0.9$, was added to the suspension with agitation. After the addition of the flocculating agent, the suspension was conditioned for 30 seconds, whereupon the agitation was discontinued and the settling time required to reduce absorption of light to half its initial value was measured. The following results were obtained.

Flocculating agent	Settling time, sec.
Polyethyleneimine	23.5
Cationic starch	25.2
Cellulose ether $MS_{hydroxyethyl}$ = 1.8 $DS_{diethylaminoethyl}$ = 0.16 $DS_{carbamoylethyl}$ = 0.15	7.8
Cellulose ether $MS_{hydroxyethyl}$ = 1.8 DS_{ethyl} = 0.9 $DS_{diethylaminoethyl}$ = 0.16	8.9

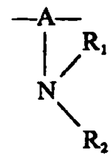
The flocculating agents of this invention have a settling time which amounts to only about $\frac{1}{3}$ of the time required for the comparison products which are conventional and recognized flocculating agents. This shows that the cellulose ethers of this invention have excellent flocculating properties and can be employed with great advantage as flocculating agents in the purification of water and sewage.

WHAT WE CLAIM IS:—

1. A method of aggregating particles wherein a suspension or colloidal solution containing solid particles is brought into contact with a tertiary nitrogen-containing cellulose ether having a degree of polymerization of 100—5000 and containing substituents of the general formula:



where a and b, which may be the same or different each is 2, 3 or 4, c is an integer from 1 to 20; m and p, which may be the same or different each is 0, 1, 2 or 3; n is 0, 1, 2, 3, 4 or 5; q is 0 or 1; A represents a hydrocarbon residue A_1 having 1 to 5 carbon atoms or A_1—O—, where A_1 is as defined above, A_1 being optionally substituted by one or more hydroxyl groups; R_1 and R_2, which may be the same or different each represents a hydrocarbon group having 1 to 10 carbon atoms, or a substituted hydrocarbon group containing 1 to 10 carbon atoms and having one or more ether linkages and/or one or more primary, secondary or tertiary amino groups, or R_1 and R_2 together with the nitrogen atom to which they are linked represents a heterocyclic ring containing one or more hetero atoms of which at least one is nitrogen; and R_3 represents hydrogen, $CONH_2$ or CN or COOH or a salt thereof, said cellulose ether being one in which the number of nitrogen atoms from the group



per anhydroglucose unit is 0.01—1.0, the average number of $CONH_2$, CN or COOH groups per anhydroglucose unit is 0 to 1.0 and the average of m+p+q is 0.5—5.0.

2. A method according to claim 1, wherein the cellulose ether is one in which the number of hydrogen atoms per anhydroglucose unit is 0.1 to 0.5.

3. A method according to claim 1 or 2, wherein the cellulose ether is one in which the average of m+p+q is 0.8—3.0

4. A method according to any one of the preceding claims, wherein the cellulose ether is one in which a and b which may be the same or different each is 2, 3 or 4, c is 1, 2, 3 or 4, m and p which may be the same or different each is 0, 1, 2 or 3; q is 0 or 1; n is 0 or 1; A represents a hydrocarbon residue containing 1 to 5 carbon atoms; R_1 and R_2 which may be the same or different each is a hydrocarbon group having 1 to 5 carbon atoms; and R_3 represents hydrogen, the average number of nitrogen atoms per anhydroglucose unit being 0.01—1.0, and the average of m+p+q being 0.5 to 3.0, per anhydroglucose unit.

5. A method according to claim 4, wherein a is 2, b is 2, c is 2, the average number of nitrogen atoms per anhydroglucose unit is 0.1—0.5 and the average of m+p+q is 0.8 to 2.0.

6. A method according to any one of the preceding claims, wherein the tertiary nitrogen-containing cellulose ether is used as a retention agent in a paper making process.

7. A method according to claim 6, wherein 10—2000 g of cellulose ether is used per ton of dry cellulose pulp.

8. A method according to claim 7, wherein 50—600 g of cellulose ether is used.

9. A method according to any one of claims 1—5, wherein the tertiary amino-containing cellulose ether is used as an aggregating agent (a) in the manufacture of sheet materials from inorganic or organic fibres, (b) in the purification of aqueous effluents, (c) in the flotation and enrichment of minerals or (d) in flocculation or precipitation in textile or foodstuff manufacture.

10. A method according to any one of the preceding claims, wherein the tertiary nitrogen-containing cellulose ether is one described in any one of Examples 1—10.

11. A method of aggregating particles according to claim 1, substantially as hereinbefore described.

12. An aggregate obtained by a process according to any one of the preceding claims.

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